



Research article

Biomass to levulinic acid: A techno-economic analysis and sustainability of biorefinery processes in Southeast Asia

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ABSTRACT

Aligned with Singapore's commitment to sustainable development and investment in renewable resources, cleaner energy and technology (Sustainable Singapore Blueprint), we report a techno-economic analysis of the biorefinery process in Southeast Asia. The considerations in this study provide an overview of the current and future challenges in the biomass-to-chemical processes with life-cycle thinking, linking the land used for agriculture and biomass to the levulinic acid production. 7–8 kg of lignocellulosic feedstock (glucan content 30–35 wt%) from agriculture residues empty fruit bunches (EFB) or rice straw (RS) can be processed to yield 1 kg of levulinic acid. Comparisons of both traditional and “green” alternative solvents and separation techniques for the chemical process were modelled and their relative energy profiles evaluated. Using 2-methyltetrahydrofuran (2-MeTHF) as the process solvent showed to approx. 20 fold less energy demand compared to methyl isobutyl ketone (MIBK) or approx. 180 fold less energy demand compared to direct distillation from aqueous stream. Greenhouse gases emissions of the major operations throughout the supply chain (energy and solvent use, transport, field emissions) were estimated and compared against the impact of deforestation to make space for agriculture purposes. A biorefinery process for the production of 20 ktonne/year of levulinic acid from two different types of lignocellulosic feedstock was hypothesized for different scenarios. In one scenario the chemical plant producing levulinic acid was located in Singapore whereas in other scenarios, its location was placed in a neighboring country, closer to the biomass source. Results from this study show the importance of feedstock choices, as well as the associated plant locations, in the quest for sustainability objectives.

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1. Introduction

There is a growing demand for “greener” products, notably those that are derived from renewable resources (Pawelzik et al., 2013). An increasing number of chemical companies are attempting to produce solvents and fine chemicals from biomass for sustainable reasons, and at the same time stop relying on fossil-based products due to the concern over the depletion of non-renewable feedstock (Biotech Industry Organization,).

Levulinic acid is a platform chemical, important intermediate for both fine chemicals and solvent production (Bozell et al., 2000; Rackemann and Doherty, 2011; Luterbacher et al., 2014). Various research and experimental studies concerning the production of Levulinic Acid (LA) from biomass have been carried out; Ya'aini et al. (Yaaini et al., 2012) for example, investigated the conversion of

glucose, EFB, and kenaf to levulinic acid over a new hybrid catalyst. They reported 55.2% yield of LA at the experimental conditions of 145.2 °C reaction temperature, 146.7 min reaction time and 12.0% of catalyst loading. Upare et al. (2013) achieved a yield of 75% LA via the selective decomposition of hexose sugars, glucose and fructose by making use of a heterogeneous graphene oxide (GO)-based catalysts with sulfonic acid (SO₃H) functional groups (GO-SO₃H). LA produced from bagasse and RS mixed with different concentrations of hydrochloride acid (HCl) in a pressurized reactor was done by Yan et al. (2008) They found that maximum yields of LA (22.8 and 23.7% for bagasse and paddy straw, respectively) was achieved with a reaction temperature of 220 °C, reaction time of 45 min and 4.45% concentration of HCl.

Lately, ionic liquids have being applied in the area of lignocellulose to LA conversion. Fu et al. (2016) produced LA via the hydrothermal decomposition reactions of cellulose, glucose, and fructose. The substrates were catalyzed by 18 types of ionic liquids with different anions. Reusability tests for [PrSO₃HMI]Cl and

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[BSO₃HmIm]HSO₄ were carried out and revealed that [BSO₃HmIm]HSO₄ can be used over four cycles without a loss of activity. In another more recent investigation, Liu et al. (Liu et al., 2018), applied acidic ionic liquid [C3SO₃Hmim]HSO₄ to catalyze lignocellulose conversion to LA. By optimizing reaction conditions, the highest yield of LA was reported as 96.6 mol% (21.6 wt%) based on the amount of C₆-sugars in the biomass raw material. Various other discussions and works have been published on the production of LA from a variety of biomass resources; among them are the comprehensive reviews provided by Pileidis and Titirici (2016) and Antonetti et al. (2016). The challenges and possible mechanisms for the transformation of carbohydrates and raw biomass into levulinic acid were highlighted by Pileidis and Titirici (2016). Antonetti et al. (Antonetti et al., 2016), discussed in their study several catalytic systems that have been developed to produce LA from waste and raw biomass.

1.1. Industrial production

Current industrial production includes synthesis from furfuryl alcohol which is subsequently converted into levulinic acid by treatment with hydrogen chloride (Hart and Kenneth, 1956; Hsu and Chasar, 1980; Klingler and Ebertz, 2000). Alternative routes include Arkenol (Cuzens and Farone, 1998), Segetis (Mullen et al., 2013), Biofine (Fitzpatrick, 1997) and other biorefinery processes in which C₆ and/or C₅ sugars from cellulosic feedstock are converted to levulinic acid and/or furfural, requiring overall less energy, solvent and chemical steps. The advantage of the biorefinery technology relies on the possibility to convert lignocellulosic material into valuable chemicals (Kamm and Kamm, 2004). This concept, which explores the potential of production high added-value bio-derived chemical products, have been explored extensively by Kruse and Dahmen (2017). Large-scale manufacturers of LA exist in China and India, but there are lack of biorefineries producing LA within the geographical boundary of Southeast Asia. This forms the basis of our research.

Although levulinic acid may be more easily purified by conversion into derivatives (i.e. esters) (Murat Sen et al., 2012), in our LCA-type approach we focused on the acid itself because of its central role in many downstream process (i.e. angelica lactone, gamma-valerolactone, 2-MeTHF, adipic acid), in order to provide the base for future studies on specific biomass-to-chemicals processes.

1.2. Objectives

The objective of this case study is two-fold. One is to investigate the environmental impacts, including energy consumption, of a biomass-to-chemical biorefinery value chain; and the other is to test the economic feasibility of the plant. In both analyses, the selection of biomass feedstock, modes of transport and plant locations will be compared.

In the techno-economic investigation we attempt to answer the questions of:

- the feasibility of setting up a biorefinery plant located in Singapore
- cost estimation involved in logistics, storage, and operating capacity

2. Materials and methods: LCA approach

Life cycle assessment (LCA) is a systematic environmental management tool applied in industry for quantifying the input-output inventory of a product system throughout its life cycle stages, and projecting the environmental performance based on a

quantified service value (known as functional unit) of the product (Khoo et al., 2016). Owing to the variety of biomass feedstock for biorefinery processes, along with the debates on the final environmental benefits or drawbacks of such systems, LCA has been increasingly used to compare various bio-based material production chains. In many cases, the focus of investigation is on the energy demands and CO₂ emissions of the life cycle stages, starting from agriculture land to the final conversion of biomass to chemicals (refer to Fig. 1).

For the techno-economic investigation, the following are considered in the LCA system:

- Different feedstock choices including cultivation and land use
- Logistics and storage
- Energy demands
- CO₂-eq emissions
- Plant capacity (20 ktonne/year)
- Costs

2.1. Case study: biorefinery model

In the past decade we observed large experimental efforts being made to test the production of lignocellulose derived bio-products, with bio-ethanol being a major object of desire of agro-industrial biomass processes (Adsul et al., 2006; Girisuta et al., 2013; Saha et al., 2013; Anwar et al., 2014). Alongside ethanol, more chemically intriguing compounds have been accessed in recent years thanks to advances in both biochemical transformations of lignocellulosic material and catalysis to upgrade and further valorize bio-products, leading to new product lines such as specialty lignins or sugar-based chemicals (Brethauer and Studer, 2015; Wu et al., 2016; Rødsrud et al., 2012). Depending on different treatment methods of lignocellulosic biomass, more than 200 valuable compounds can be obtained, but important factors need to be considered in production scale scenarios such as collection and storage logistics as well as biomass availability (Isikgor and Becer, 2015; Dusselier et al., 2014). Progresses towards optimization of biomass to chemicals process have been reported in the literature (Amore et al., 2016). Such research efforts attempt to generate bio-based chemicals that are of good economic value, are sustainable and have the potential to reduce the chemical industry's reliance on petroleum (Dodds and Gross, 2007). Lignocellulosic biomass is primarily made of the three most abundant polymers in nature: cellulose, hemicelluloses and lignin. In the first chemical step, lignin is separated from cellulose and hemicellulose and either burned (to furnish energy) or used for other applications (Nägele et al., 2002). Acid hydrolysis of hemicellulose and cellulose produces C₅ and C₆ sugars which are subsequently converted into furfural and/or levulinic acid, depending on the specific operating conditions of the process (Sabesan and Spado, 2013). In accordance with existing data (Khoo et al., 2015), we estimated that 6.6–7.6 kg of biomass (glucan content 30–34 wt%) are required for the production of one kg of levulinic acid (Fig. 2).

2.2. Feedstock choices

Indonesia and Malaysia are the two biggest producers of crude palm oil and kernel palm oil in the world. After the milling process, abundant quantity of empty fruit bunches are produced as waste. In the context of Southeast Asia another type of lignocellulosic biomass available in large quantity is rice straw. Thailand is a big producer of rice and similar considerations for the rice straw can be done. In our study we analyzed the biorefinery process with sustainability objectives in mind, taking into consideration the three

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